
Highlights from Recent Literature

1 ANALYTICAL

1.1 A Methodology for Determining the Department of Cyanide Losses in Gold Plants

Cyanide is a major cost centre in gold processing plants, and establishing the causes of cyanide loss can result in significant savings. The department of cyanide is complex, and can include volatilization, precipitation, complexation with metals, oxidation to cyanate or ammonia, and reaction with sulfide minerals to form thiocyanate. In this paper, by M.D. Adams of Lakefield Orestest, Kewdale, Australia *Miner. Eng.*, 2001, **14**(4), 383-390, a simple methodology is provided using thermodynamic constants and solution analyses, to determine the speciation and department of cyanide in gold plant liquors and solids. Samples with different ore mineralogies and chemistries were assayed, and compared with results obtained by direct measurement using several techniques.

Meaningful analysis of cyanide in the presence of copper is obtained, because the changing equilibrium levels of the copper cyanide complexes are taken into consideration in the analysis. Thiocyanate can account for a considerable amount of the cyanide consumed. The loss of cyanide due to volatilization can be significant in highly saline solutions; and the adsorption of cyanide and thiocyanate onto solids can also be important, depending on the mineralogy involved.

2 CATALYSIS

2.1 Iridium-Gold Carbonylation Catalysts

A carbon-supported solid catalyst suitable for the vapour-phase carbonylation of lower aliphatic alcohols (especially methanol), ethers, esters, and ester-alcohol mixtures to produce carboxylic acids and/or their esters includes an effective amount of iridium and gold associated with a solid carbon support, and a halogen promoter, and has been patented by J.R. Zoeller, A.H. Singleton G.C. Tustin and D.L. Carver of the Eastman Chemical Company, US Patent 6177380 B1 (23 January 2001). The halogen promoter component of the catalyst is preferably vaporous, thus providing a two-phase catalyst system. Thus, activated carbon particles were impregnated with an aqueous solution of HAuCl_4 , dried at 300°C , impregnated with an aqueous solution of IrCl_3 , and dried at 300°C to give a catalyst. A 7:3 (wt) MeOH-MeI mixture at 12 mL/h was evaporated and passed over 0.5 g of the catalyst, which had been pre-equilibrated to 240°C and 250 psia, together with 25 cm^3/min hydrogen and 100 cm^3/min carbon monoxide. The

reaction produced acetic acid and methyl acetate combined at a rate of 227 mol/kg catalyst per h, compared with 56 and 97 mol/kg catalyst per h, respectively, for catalysts containing only gold or only iridium in equivalent amounts.

2.2 Supported Gold Catalysts Prepared from a Gold Phosphine Precursor and As-Precipitated Metal-Hydroxide Precursors: Effect of Preparation Conditions on the Catalytic Performance

Supported gold catalysts which are highly active for low-temperature carbon monoxide oxidation were prepared by using $\text{AuPPh}_3\text{NO}_3$ complex as a gold-metal precursor and wet, as-precipitated iron hydroxide and titanium hydroxide as support precursors. The effects of catalyst preparation conditions on the performance for low-temperature carbon monoxide oxidation have been studied by A.I. Kozlov, A.P. Kozlova, K. Asakura, Y. Matsui, T. Kogure, T. Shido and Y. Iwasawa, Department of Chemistry, Graduate School of Science, The University of Tokyo, Japan, *J. Catal.*, 2000, **196**(1), 56-65.

Metal-hydroxide precipitation conditions and heating rates of temperature-programmed calcination significantly altered the performance of the supported gold catalysts. Changes in the activities of both Au/Fe oxide and Au/Ti oxide catalysts originated mainly from changes of the gold particle size distribution. It was also found that states of the mesoporous support precursors upon attaching the gold precursor onto them and during the temperature-programmed calcination appeared to be of great importance in obtaining dispersed gold nanoparticles on oxide surfaces.

2.3 Catalytic Combustion of Volatile Organic Compounds on Gold/Iron Oxide Catalysts

Catalytic oxidation of 2-propanol, methanol, ethanol, acetone and toluene was studied by S. Minico, S. Scire, C. Crisafulli, R. Maggiore and S. Galvagno, Dipartimento di Scienze Chimiche, Università di Catania, Italy, *Appl. Catal., B*, 2000, **28**(3,4), 245-251, on coprecipitated Au/ Fe_2O_3 catalysts in the presence of an excess of oxygen. Catalysts were very active in the oxidation of volatile organic compounds (VOCs). The high activity of these systems has been related to the capacity of highly dispersed gold to weaken the Fe-O bond thus increasing the mobility of the lattice oxygen which is involved in oxidation of the VOCs, probably through a Mars-van Krevelen reaction mechanism.

2.4 Influence of Gold Content in Nickel Catalysts on the Course of the Carbon Monoxide + Nitric Oxide Reaction

W. Cwikla and D. Nazimek of the Faculty of Chemistry, University of Marie Curie-Skłodowska, Lublin, Poland, *Technol. Chem. Przelomie Wiekow*, 2000, 627-630, have described the interesting results obtained by the addition of gold to nickel catalysts, arising from the large difference in the heats of chemisorption of NO and CO on these metals. The aim of the present research was to examine the course of NO reduction by CO and to follow the changes in the activity and selectivity of the process for alloys of varied Ni-Au composition. The results of adsorption measurements indicated that changes in the surface which binds hydrogen in Ni-Au catalysts, produced by the presence of gold, may be seen as a consequence of an overlapping of two mutually opposed factors, *ie* the increase in the rate of NiO reduction and surface segregation of gold. The introduction of even a small quantity of gold produces a change in the energy character of nickel centres. With these nickel-gold systems the reaction rate is limited by dissociative NO chemisorption.

2.5 Highly Dispersed Supported Gold Catalysts for Methanol and Formaldehyde Oxidation

In order to develop a catalyst system for the complete removal of the unburned methanol and formaldehyde in exhaust gas from methanol-fuelled vehicles, the activity of various supported metal oxides or gold catalysts has been studied using a conventional flow reactor. It is reported by H.-G. Ahn, D.-A. Park, S.-C. Jung, M.-C. Chung and B.H. Kim, Department of Chemical Engineering, Sunchon National University, S. Korea, *Kongop Hwahak*, 2000, 11(5), 529-534, that the activity of the gold catalysts for methanol and formaldehyde oxidation was much higher than that for supported metal oxide catalysts, *eg* $\text{MoO}_3/\text{Al}_2\text{O}_3$. The order of the activity of gold catalysts for those prepared by deposition precipitation was greater than for coprecipitation which was greater than for impregnation. Gold particles on Co_3O_4 were more active than on Al_2O_3 . In particular, methanol was completely oxidized to carbon dioxide and water. The reaction mechanism proposed is that the oxygen atom dissociated on the active site reacts with the methanol or the intermediates adsorbed on the support adjacent to active sites, and then gold particles promote the dissociative adsorption of oxygen.

3 CHEMISTRY

3.1 Manufacture of Gold Compound Solution

H. Sasaki and M. Kida of Tanaka Noble Metal Industrial Co Ltd, Japan, Japanese Patent 2001048537 A2, 20 February 2001 have described the manufacture of a solution of gold compound from HAuCl_4 , neutralizing that by an alkali metal hydroxide

(*eg*, KOH) solution, water washing precipitates (*eg* $\text{Au}(\text{OH})_3$), and dissolving this using an alkali metal hydroxide to obtain the solution of the gold compound. An HClO -containing compound (*eg* KClO) is added to the gold compound solution to suppress reduction and precipitation of gold. The gold compound solution can be used for preparing gold catalyst, or as a gold plating liquid, *etc*. The final product was essentially a solution of $\text{KAu}(\text{OH})_4$.

3.2 Uptake of Au(III) Ions by Aluminium Hydroxide and their Spontaneous Reduction to Elemental Gold (Au^0)

The behaviour of AuCl_4^- ions during the formation of aluminium hydroxide at pH 6 has been studied by T. Yokoyama, Y. Matsukado, A. Uchida, Y. Motomura, K. Watanabe and E. Izawa of the Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, Japan, *J. Colloid Interface Sci.*, 2001, 233(1), 112-116. With an increase in sodium chloride concentration, the content of gold taken up by the aluminium hydroxide decreased, suggesting that chloro-hydroxy complexes of Au(III) ion were taken up due to the formation of Al-O-Au bonds. It was unexpectedly found that the Au(III) ions taken up were spontaneously reduced to Au^0 without addition of a specific reducing reagent and then colloidal gold particles were formed. The mechanisms for the uptake of Au(III) ions by aluminium hydroxide and for their spontaneous reduction are discussed.

3.3 Polynuclear Gold Complexes with Bridging Selenido Ligands. Theoretical Studies of Gold-Gold Interactions

S. Canales, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna and F. Mendizabal of the Departamento de Química Inorgánica Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, Spain, *Organometallics*, 2000, 19(24), 4985-4994, have shown that $[\text{Se}(\text{AuPPh}_3)_2]$ and $[\text{Se}(\text{Au}_2\text{dppf})]$ are good precursors for the synthesis of highly auroated Se-centered derivatives. Thus the reaction of $[\text{Se}(\text{AuPPh}_3)_2]$ with various molar ratios of $[\text{Au}(\text{OTf})\text{PPh}_3]$ affords the homoleptic species $[\text{Se}(\text{AuPPh}_3)_n](\text{OTf})_{n-2}$ ($n = 3-6$). Similarly, the treatment of $[\text{Se}(\text{Au}_2\text{dppf})]$ with various stoichiometric ratios of $[\text{Au}_2(\text{OTf})_2(\mu\text{-dppf})]$ gives polynuclear $[(\text{Au}_2\text{dppf})\{\text{Se}(\text{Au}_2\text{dppf})\}_2](\text{OTf})_2$, $[\text{Se}(\text{Au}_2\text{dppf})_2](\text{OTf})_2$, and $[\text{Se}(\text{Au}_2\text{dppf})_3](\text{OTf})_4$. $[\text{Au}\{\text{Se}(\text{AuPPh}_3)_2\}_2]\text{ClO}_4$ and $[\text{Au}\{\text{Se}(\text{Au}_2\text{dppf})\}_2]\text{ClO}_4$ were obtained by reaction of the precursors with $[\text{Au}(\text{tht})_2]\text{ClO}_4$ in a molar ratio of 2:1. Some of these derivatives were characterized by x-ray diffraction studies and show unusual geometries, associated with Au-Au interactions. The latter were studied theoretically using $[\text{Se}(\text{AuPPh}_3)_n]_{(n-2)}^+$ ($n = 2-6$) models at the HF and MP_2 levels with quasi-relativistic pseudopotentials. There is good agreement between experimental and theoretical geometries.

3.4 Mixed Valent Gold Oxides: Syntheses, Structures, and Properties of $\text{Rb}_5\text{Au}_3\text{O}_2$, $\text{Rb}_7\text{Au}_5\text{O}_2$ and $\text{Cs}_7\text{Au}_5\text{O}_2$

Title compounds are the first examples of mixed valent phases containing gold in the oxidation states +1 and -1. A.-V. Mudring, J. Nuss, U. Wedig and M. Jansen, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany, *J. Solid State Chem.*, 2000, **155**(1), 29-36, report that they have a combination of distinctive structural features of Au(I) oxides and aurides: for Au^+ a typical linear coordination by oxygen is found and the surroundings of Au^- bear a close resemblance to the binary 1:1 aurides. In consequence, the overall structures of $\text{Rb}_5\text{Au}_3\text{O}_2$ and $\text{M}_7\text{Au}_5\text{O}_2$ can be described as intergrowths of M_3AuO_2 and MAu ($\text{M} = \text{Rb}, \text{Cs}$), constituting members of a homologous series $[\text{MAu}]_n[\text{M}_3\text{AuO}_2]$ with $n = 2$ and 4, respectively. The crystal chemistry evidence for the valence states assumed, also confirmed by Mössbauer spectroscopy, is supported by various band structure calculations (Hartree-Fock and density functional) clearly indicating the coexistence of two different oxidation states.

The compounds were synthesized by reacting binary aurides MAu and alkali monoxides M_2O ($\text{M} = \text{Rb}, \text{Cs}$) with elemental gold in the required stoichiometric amounts. A further astonishing parallel to the chemistry of halogens was thus revealed. Like these, gold disproportionates upon interaction with bases.

3.5 Molecular Multinuclear Gold(I) Complexes

V. W.-W. Yam and E. C.-C. Cheng, of the Department of Chemistry, The University of Hong Kong, P.R. China, *Angew. Chem., Int. Ed.*, 2000, **39**(23), 4240-4244 have written a review, with 37 references, on recently reported multinuclear gold(I) complexes and clusters (see also V. W.-W. Yam and E. C.-C. Cheng, *Gold Bull.*, 2001, **34**, 20-23).

3.6 Syntheses and Characterization of Gold(III) Tetradentate Schiff Base Complexes

Some Au(III) complexes containing tetradentate Schiff base ligands have been synthesized and characterized by S.L. Barnholtz, J.D. Lydon, G. Huang, M. Venkatesh, C.L. Barnes, A.R. Ketrang and S. Jurisson, Department of Chemistry and Missouri University Research Reactor, University of Missouri, Columbia, USA, *Inorg. Chem.*, 2001, **40**(5), 972-976. Gold(III) forms four-coordinate square planar complexes with these ligands. These complexes were characterized by their elemental analyses and UV-visible, IR, NMR, and mass spectra. Preliminary radiochemical studies with Au-198 show that these complexes, eg $[\text{Au}(\text{sal}_2\text{pn})]\text{Cl}$ ($\text{sal}_2\text{pn} = \text{N}, \text{N}'\text{-propylenebis(salicylideneimine)}$), are also formed at the tracer level from $(\text{Bu}_4\text{N})[^{198}\text{AuCl}_4]$.

4 COATINGS, FILMS, MEMBRANES AND WIRES

4.1 The Early Stages of Plastic Yielding in Polycrystalline Gold Thin Films

K. Owusu-Boahen and A.H. King, Department of Materials Science and Engineering, State University of New York at Stony Brook, USA, *Acta Mater.*, 2001, **49**(2), 237-247, have described transmission electron microscope observations of the effects of stress in polycrystalline gold thin films. The films exhibit a very strong {111} fibre texture, and are loaded in biaxial tensile stress. Under these conditions, each grain exhibits the same Schmid factor, within a very small variance. Despite the identical loading conditions and resolved shear stresses from grain to grain, they observed that yield was isolated in only a few grains. Yield initiates only at specific triple junctions, and the conditions required for a triple junction to be active in this manner were defined. The required conditions for yield to occur at a triple junction include (1) an appropriate slip-plane inclination relative to the grain boundaries at the junction; and (2) at least one grain boundary of appropriate character, adjacent to the slip plane specified in (1).

4.2 Assembling Gold Nanoparticles as Nanostructured Films using an Electrophoretic Approach

N. Chandrasekharan and P.V. Kamat, Notre Dame Radiation Laboratory, IN, USA, *Nano Lett.*, 2001, **1**(2), 67-70, describe how a three-dimensional array of gold nanoparticles was assembled on a nanostructured TiO_2 template by subjecting the colloidal gold suspension to a d.c. electric field (50-500 V). By controlling the concentration of gold colloids in toluene and the applied voltage, it is possible to control the thickness of the nanostructured gold film without inducing aggregation effects. As indicated by AFM, these gold films are highly porous and consist of a nanoparticle assembly of fairly uniform size. The surface plasmon characteristics observed in these nanostructured gold films suggest that the particles retain the identity of individual nanoparticles.

4.3 Focused Electron Beam Induced Deposition of Gold

Codeposition of hydrocarbons is a severe problem during focused electron beam writing of pure metal nanostructures. When using organometallic precursors, a low metal content carbonaceous matrix embedding and separating numerous nanosized metal clusters is formed.

In this work, I. Utke, P. Hoffmann, B. Dwir, K. Leifer, E. Kapon and P. Doppelt, of the Microengineering Department, EPFL-DMT-IOA, Swiss Federal Institute of Technology, Lausanne, Switzerland, *J. Vac. Sci. Technol.*, B, 2000, **18**, 3168-3171, present a new and easy approach to obtain high purity gold lines: ie the use of inorganic PF_3AuCl as a precursor.

Electrical resistivities as low as 22 $\mu\Omega\text{-cm}$ at 295 K (ten times the bulk gold value) were obtained. This is to the authors' knowledge the best value for focused electron beam deposition obtained from the vapour phase so far. No special care was taken to prevent hydrocarbon contamination. The deposited nanostructure consists of gold grains varying in size and percolation with beam parameters.

5 COLLOIDS AND NANOTECHNOLOGY

5.1 Size-controlled Colloidal Gold Nanoparticles Dispersed in Organic Solvents

The preparation of well-size-controlled colloidal gold nanoparticles in an organic solvent has been investigated by G. Tsutsui, S. Huang, H. Sakaue, S. Shingubara and T. Takahagi of the Department of Electrical Engineering, Hiroshima University, Japan, *Jpn. J. Appl. Phys., Part 1*, 2001, **40**(1), 346-349. After the preparation of aqueous colloidal gold particles, they changed the solvent to an organic one. This technique is required to enable a chemical reaction between the gold particles and hydrophobic molecules, since a colloidal gold solution is typically prepared in water using a reduction process. The stability of the gold particle suspension was also investigated, and found to decrease in the sequence of water, ethanol, chloroform, and benzene.

5.2 Spectroscopic Determination of the Melting Energy of a Gold Nanorod

S. Link and M.A. El-Sayed of the Laser Dynamics Laboratory, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA, USA, *J. Chem. Phys.*, 2001, **114**(5), 2362-2368, have demonstrated that gold nanorods in colloidal solution can be melted into spherical nanoparticles by excitation with intense femtosecond laser pulses of appropriate energy. The threshold of the laser pulse energy for the complete melting of the nanorods with a mean aspect ratio of 4:1 in solution is determined by observing the change in the absorption intensity of the longitudinal absorption band (measure of the rod concentration) at 800 nm with increasing number of laser pulses of known energy. The number of laser pulses needed to reduce the band intensity (rod concentration) by 1/e of its initial value was determined as the laser energy per pulse increases.

A simple analysis using the determined threshold energy and the nanorod concentration showed that it takes an average of *ca* 60 fJ to melt a single gold nanorod. Experiments using 820 nm as well as 410 nm femtosecond laser pulses yield similar values, indicating that the laser induced shape transformation of the nanorods is independent of the irradiation wavelength and that this process is therefore photothermal in origin.

5.3 The Nucleation and Growth of Gold on Silica

K. Luo, D.Y. Kim and D.W. Goodman, Department of Chemistry, Texas A&M University, College Station, TX, USA, *J. Mol. Catal. A: Chem.*, 2001, **167**(1-2), 191-198, have studied the nucleation and growth of gold clusters supported on $\text{SiO}_2/\text{Mo}(110)$ using XPS, low energy ion scattering, and temperature programmed desorption. Stoichiometric ultrathin SiO_2 films were synthesized and characterized by Auger electron spectroscopy and XPS. At 300 K, the growth mode of gold at fractional monolayer coverages is quasi-2D; at higher coverages, 3D growth was found with no evidence of a significant chemical interaction between gold and silica. Annealing $\text{Au}/\text{SiO}_2/\text{Mo}(110)$ to 1000 K led to sintering of the gold clusters. The desorption activation energies for gold coverages of <0.2 monolayer equivalent were determined by TPD to be significantly lower than the sublimation energies found for higher coverages of gold clusters and for bulk gold.

5.4 Nonlinear Optical Properties of Molecularly Bridged Gold Nanoparticle Arrays

Hyper-Rayleigh scattering spectroscopy has been used by J.P. Novak, L.C. Brousseau, F.W. Vance, R.C. Johnson, B.I. Lemon, J.T. Hupp and D.L. Feldheim, Department of Chemistry, North Carolina State University, Raleigh, NC, USA, *J. Am. Chem. Soc.*, 2000, **122**(48), 12029-12030, to measure collective nonlinear optical properties in gold nanoparticle arrays. Large responses were observed. Both symmetry and distance are important in determining the nonlinear optical behaviour of gold nanoparticles connected by molecular bridges.

5.5 Fabrication of Nanostructures by Hydroxylamine Seeding of Gold Nanoparticle Templates

Hydroxylamine-seeding of colloidal gold particles was used by S. Meltzer, R. Resch, B.E. Koel, M.E. Thompson, A. Madhukar, A.A.G. Requicha and P. Will, Laboratory for Molecular Robotics, University of Southern California, Los Angeles, USA, *Langmuir*, 2001, **17**(5), 1713-1718, to fabricate gold nanostructures on a silica substrate. Gold nanoparticles (15 nm diameter) were randomly deposited on a silica surface that had been modified with aminopropyltrimethoxysilane (APTS). The nanoparticles were then manipulated using a scanning force microscope (SFM) tip to produce 1-dimensional templates for gold deposition. The authors demonstrate the utility of this approach by fabricating a gold nanowire by using 13 nanoparticles as a template. This approach was also used to fabricate nanostructures in a small gap between two gold electrodes. Particles were pushed into the gap, and then gold deposition was used to connect the particles and the electrodes.

6 ELECTROCHEMISTRY

6.1 Gold Plating

Gold has been applied to surfaces of electronic components by electroplating, thermal decomposition of a screen-printed paste, vacuum deposition or thermal decomposition of an organometallic compound, or by mechanical rolling of inlay material. The plating solution usually contains $\text{KAu}(\text{CN})_2$ together with substances for the stabilization of the conductivity and buffers. Grain refining additives such as As^{3+} , Ti^{2+} , and Pb^{2+} are added in the plating solutions at low concentrations. Post-plating treatments, environmental status, health impact, and trends are outlined in this review by A. Blair, *Plat. Surf. Finish.*, 2000, **87**(8), 46, 48.

6.2 Electrocatalytic Oxidation of Phenol at Potentiodynamically Preanodized Gold Electrodes in Alkaline Medium

The catalytic effect of potentiodynamically grown oxide films on gold during the electrooxidation of phenol in an alkaline medium has been studied by P.I. Iotov and S.V. Kalcheva, University of Chemical Technology and Metallurgy, Sofia, Bulgaria, *Bull. Electrochem.*, 2000, **16**(9), 407-414. The α - and β -oxides grown during the anodization provide redox mediator systems. Other advantages of the preoxidized gold electrode are connected with hindering the polymerization and easier *in-situ* removal of the polymer film. A tentative mechanism based on the experimental results, reference data and in particular the incipient hydrous oxide/adatom mediator model of electrocatalysis was proposed.

7 ELECTRONICS

7.1 Proximity Effect and Multiple Andreev Reflections in Gold Atomic Contacts

The electronic transport properties of gold point contacts with superconducting aluminum leads have been investigated by E. Scheer, W. Belzig, Y. Naveh, M.H. Devoret, D. Esteve and C. Urbina, Physikalisches Institut, Universität Karlsruhe, Germany, *Phys. Rev. Lett.*, 2001, **86**(2), 284-287. The modifications induced by the proximity effect in the quasiparticle density of states at the contact region are measured by tunnel spectroscopy. The theory of transport through multiple Andreev reflections is extended to incorporate these effects and used to determine the number and transmission coefficients of the conduction channels in the contact regime.

7.2 Fabrication Methods for Gold Nanocluster Devices

A.W. Snow, M.G. Ancona, W. Kruppa, D. Park, J.B. Boos and G.G. Jernigan of the Naval Research Laboratory, Washington, DC, USA, *Mater. Res. Soc. Symp. Proc.*, 2001, **582**(Molecular Electronics), H12.5/1-H12.5/6, have studied the deposition chemistry of hexanethiol-stabilized gold nanoclusters self-assembled on gold and silica surfaces by reaction with a series of α,ω -alkanedithiols using XPS and electrical measurements. Testing of micron-scale devices shows that high conductivity is achieved only for a narrow range of dithiols and with a sharp efficiency threshold. Nanoscale devices exhibit similar behaviour though with much evidence of 'granularity' in the deposition.

7.3 Room-Temperature Single Electron Charging in Gold Nanoparticle Networks Formed on Biopolymer Templates

The current-voltage characteristics of gold nanoparticle-biopolymer networks at room temperature have been studied by M.N. Wybourne, L. Clarke, C.A. Berven, J.E. Hutchison, L.O. Brown and J.L. Mooster of the Department of Physics and Astronomy, Dartmouth College, Hanover, NH, USA, *Mater. Res. Soc. Symp. Proc.*, 2001, **582**(Molecular Electronics), H13.4/1-H13.4/6. Above a threshold voltage, the current-voltage relation is almost linear. From the current-voltage scaling above threshold, the one-dimensional regions of the network dominate the transport. Periodic features in the conductance are found in many samples.

Both the threshold voltage and the conductance features occur at voltages much greater than expected for the capacitance of the nanoparticles. Possible explanations for the structure are considered.

7.4 Metal-Insulator Transition in Stable One-Dimensional Arrangements of Single Gold Atoms

The atomic arrangement and conductance during the separation process of gold point contacts were simultaneously observed *in-situ* by high-resolution TEM microscopy (T. Kizuka, S. Umehara and S. Fujisawa, Department of Applied Physics, School of Engineering, Nagoya University, Japan, *Jpn. J. Appl. Phys.*, Part 2 (2001), **40**(1A/B), L71-L74). One-dimensional arrangements of gold single atoms, *ie*, atomic wires, appeared between two tips at the point contacts. They were stable when their length was increased up to 2.6 nm. The interatomic distance of the wires was 0.25-0.31 nm. It was found that a metal-insulator transition occurs in the wires.

MATERIALS SCIENCE

8.1 Production of a Purple Pigment Based on Colloidal Gold

Z. Gasiorowski and K. Kazimierz of Mennica Panstwowa S.A., Poland, *Polish Patent* 177180 B1 (29 January 1999) describe how the colloidal gold pigment is produced from AuCl_3 or HAuCl_4 by reduction by using an anhydrous or hydrated Sn^{2+} salt and/or its solution in the presence of an anhydrous or hydrated Sn^{4+} salt and/or its solution. The reaction is carried out in the presence of a neutral solid reaction support (eg. SiO_2) with a surface area of $>1,000 \text{ cm}^2/\text{g}$. The resulting pigment is suitable for decoration of ceramics.

8.2 Preparation of Gelatin Layer with Gold Clusters in Photographic Film

A photographic process involving gold has been described by K. Kuge, M. Arisawa, N. Aoki and A. Hasegawa of the Department of Information and Imaging Sciences, Faculty of Engineering, Chiba University, Japan, *Jpn. J. Appl. Phys.*, Part 1, 2000, **39**(12A), 6550-6554. A gelatin layer film with gold clusters is produced by taking advantage of the photosensitivity of silver halide photography. Through exposure, silver latent-image specks, which are composed of several reduced silver atoms, are formed on the surface of silver halide grains in the photographic film. As the latent-image specks act as a catalyst for redox reactions, reduced gold atoms are deposited on the latent-image specks when the exposed film is immersed in a gold(I) thiocyanate complex solution for 5-20 days. Subsequently, when the silver halide grains are dissolved and removed, the gelatin layer film with gold clusters remains. The film produced by this method is purple and showed an absorption spectrum maximum of *ca* 560 nm as a result of plasmon absorption. The clusters continued to grow with immersion time, and the growth rate increased as the concentration of the gold complex solution was increased. The cluster diameter increased from 20 to 100 nm. By this method, it is possible to produce a gelatin film of a large area with evenly dispersed gold clusters, and since it is produced only on the exposed area, pattern forming is also possible.

9 MEDICAL AND DENTAL

9.1 Magnetic-Resonance-Compatible Balloon-Expandable Endoprosthesis (MR Stent) made from a High-Gold-Content Alloy

A balloon-expandable endoprosthesis, consisting of the following high-gold-content alloy (data in mass per cent): Au 70.0, Pt 4.4, Pd 2.0, Ir 0.1, Ag 13.5, Cu 8.8 and Zn 1.2, with other metals altogether under 0.05% and a material density of 15.7 g/cm^3 ; and a wire structure, being cut from a circular cylinder with given diameter and wall thickness by means of

laser technology has been patented by A. Rübber (German Patent DE 29914244 U1 (8 February 2001)).

9.2 Gold and Palladium Burden from Dental Restoration Materials

From 81 volunteers (16 without dental restorations, 65 with gold crowns or inlays) samples of saliva before and after chewing gum, were analysed for gold and palladium. G. Drasch, C. Muss and G. Roider of the Institut für Rechtsmedizin der Ludwig-Maximilians-Universität München, Germany, *J. Trace Elem. Med. Biol.*, 2000, **14**(2), 71-75, report that the gold concentration in all analysed biomonitors correlates significantly with the number of teeth with gold restorations. Persons with gold restorations show maximal gold and palladium concentrations, 102-103 times higher than the background burden.

The calculated maximal daily gold load in saliva (1.38 mg Au per day) reaches the range of an oral gold therapy for rheumatoid arthritis with 6 mg Auranofin (= 1.74 mg Au per day).

9.3 Dental Material Containing at Least 98% gold

This patent (U.K. Rabe, Degussa-Huls, Austria, German Patent DE 10039168, 22 March 2001) covers dental material that contains at least 98wt% gold and at least one of the following metals: rhodium, iridium, ruthenium, platinum, palladium, silver, rhenium or their combination. The preferred alloy contains 99 wt% gold and 1 wt% rhodium. The alloy can be blended with low and high melting point dental ceramics and resins and used as dental crowns.

10 METALLURGY

10.1 Kinetic Electron Emission from Clean Polycrystalline Gold Induced by Impact of Slow C^+ , N^+ , O^+ , Ne^+ , Xe^+ , and Au^+ ions

Ion-induced kinetic electron emission is commonly attributed to collisions of an energetic projectile with quasi-free electrons, and to the promotion of atomic levels in binary collisions of the projectile with atomic particles in the solid. The contribution of the promotion processes to the electron emission has been estimated theoretically for all studied systems from MO correlation diagrams (J. Lorincik, Z. Sroubek, H. Eder, F. Aumayr and H. Winter, Academy of Sciences of the Czech Republic, J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, **62**(23), 16116-16125).

As quasi-free electron collisional excitations have a sharp threshold at relatively high velocities of the projectiles, their contribution to the electron emission at lower impact velocities should be negligible. The authors show, however, that the partial

localization of the quasi-free electrons due to the presence of the solid surface ‘washes out’ this sharp threshold. This can lead to one-electron excitations at low impact velocities that may be more significant than excitations due to promotion. At the lowest impact velocities, the electron emission yields conspicuously level off in some of the cases studied. Such behaviour cannot be reconciled with any existing one-electron model (including the one proposed here), as they all predict a rapid decrease of the electron emission with decreasing impact velocity. In this paper, the authors interpret the levelling-off of the yield in terms of a many-electron excitation mechanism, based on the assumption of spatial and temporal localizations of electronic excitation in the impact zone.

The models discussed in this paper are compared with experimental data on kinetic electron emission from polycrystalline gold bombarded by C^+ , N^+ , O^+ , Ne^+ , Ne^0 , Xe^+ , and Au^+ , with kinetic energies below ca 15 keV, and perpendicular incidence on the surface.

10.2 Gold Alloy for Fine Wires in Ball-Tip Bonding of Semiconductor Devices

A patent on gold alloys for heat-resistant fine wires suitable for ball-tip bonding of semiconductor devices has been filed by T. Uno and K. Tatsumi of the Nippon Steel Company, Japan, US Patent 6210637 (3 April 2001). The alloy contains: (a) Mn 0.005-0.3 and Pd 0.005-1.0%; (b) one of Pt, Ag, and/or Cu at 0.01-1.0%; and (c) one of Ca, Be, In, and/or rare earth metals at 0.0005-0.05%. The microalloyed gold wires show decreased corrosion after heating, and increased long-term reliability when bonded to aluminium electrodes in semiconductor circuits. A typical gold alloy for ball-bonding wires having 25 μm diameter is stable for 200 h heating at 200°C in a resin-sealed semiconductor device and contains Mn 0.04, Pd 0.08, Pt 0.02, and Ag 0.03%. Microalloyed gold containing Mn 0.002 and Pd 0.05% has decreased strength and a tendency to corrode. See also Ch. Simons, L. Schr ppler and G. Herklotz, *Gold Bull.*, 2000, **33**(3), 89-96; and C.W. Corti, *Gold Bull.*, 1999, **32**(2), 39-47.

11 REFINING

11.1 Thiosulfate Leaching of Gold

This review, covering many references, was written by M.G. Ayllmore and D.M. Muir of the CSIRO Division of Minerals, Bentley, Australia, *Miner. Eng.*, 2001, **14**(2), 135-174. The ammoniacal thiosulfate leaching process for gold and silver

extraction has been reviewed in terms of leaching mechanism, thermodynamics, thiosulfate stability, and gold recovery options. The application to different ore types and process options are also discussed. The thiosulfate leaching process is catalysed by copper and has several advantages over the conventional cyanidation process. Thiosulfate leaching can be considered a non-toxic process, the gold dissolution rates can be faster than conventional cyanidation and, due to the decreased interference of foreign cations, high gold recoveries can be obtained from the thiosulfate leaching of complex and carbonaceous-type ores. While difficulties remain to be overcome, thiosulfate leaching has considerable potential as an effective and less hazardous procedure for gold and silver extraction from auriferous ores.

11.2 Environmental Performance of Oxidative Pre-Treatments in the Extraction of Gold

G. Andari, F.A. Roddick and C. Swaminathan of the Department of Chemical and Metallurgical Engineering, RMIT University, Melbourne, Australia, *Publ. Australas. Inst. Min. Metall.*, 2000, **5/2000**(MINPREX 2000), 139-146 have included many references in this review. As remaining gold deposits tend to become more refractory, some form of oxidative pretreatment involving hydro- or pyrometallurgy is necessary to maintain high metal recoveries. These pretreatments include pressure oxidation, bio-leaching, or roasting. In the past, the primary criterion for selection of oxidative pretreatment relied mainly on the extent of gold recovery and relative economics.

In this study, a different approach has been adopted, *ie* the quantitative determination of environmental performance of the oxidative pre-treatment processes bio-leaching, roasting, and pressure oxidation, to assess which had the least impact on the environment. The decreasing order of contribution to the environmental index was found to be acidification potential, toxicity, resource depletion, solid waste generation and greenhouse enhancement for bio-leaching and pressure oxidation; whereas it was acidification potential, solid waste generation, toxicity, resource depletion and greenhouse enhancement for roasting.

This study demonstrated the potential for the development of a predictive tool which could be used in determining the environmental performance, and thus the selection, optimization, and improvement of pre-oxidation processes for least impact on the environment.